THIS PRESENTATION DOES NOT CONTAIN ANY PROPRIETARY, CONFIDENTIAL, OR OTHERWISE RESTRICTED INFORMATION

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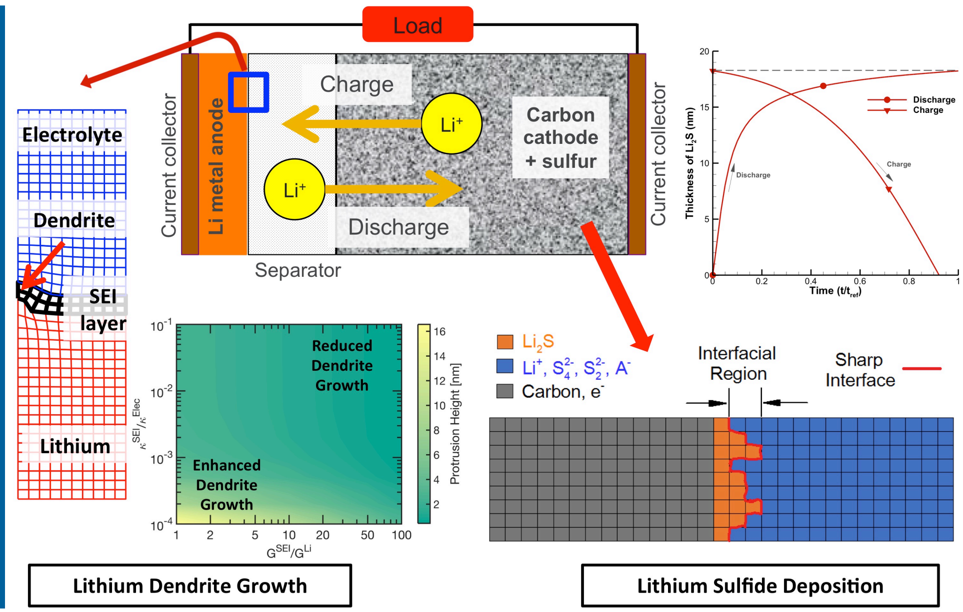
ELECTRODE MATERIALS DESIGN AND FAILURE PREDICTION



VENKAT SRINIVASAN

Argonne National Laboratory, Lemont, IL

Project ID: **BAT309**

Date: June 18th – 21th, 2018
Location: Arlington, VA

OVERVIEW

Timeline

- Project start date: October 2016
- Project end date: September 2019
- Percent complete: 50%

Barriers

- Barriers addressed
  - Dendrite growth on lithium metal with SEI layer
  - Low power capability and cycle life of lithium-sulfur batteries

Budget

- $430k/year
  - 0.1 FTE Staff Scientist
  - 1.5 FTE Postdoc

Partners

- Nitash Balsara (LBNL)
- Kenneth Higa (LBNL)
- Advanced Light Source (LBNL)
- Shrayesh Patel (U. of Chicago)

RELEVANCE

Objectives:

- Investigate the impact of solid electrolyte interphase (SEI) layer on the growth of dendritic protrusions
  - Elucidate the effects of diffusivity and conductivity of lithium through the SEI layer on overall dendrite growth process
  - Understand the impact of SEI mechanical stiffness on prevention of lithium dendrite growth

- Elucidate the deposition mechanism and deposit morphology observed on top of carbon substrate in lithium sulfur battery cathodes
  - Develop phase-field based microscale models capable of capturing the appropriate lithium sulfide deposition mechanism
  - Understand morphology of precipitates and devise strategies to minimize the surface passivation

MILESTONES

- Understand the proper stress state within lithium dendrites (December, 2016).

Completed

- Investigate the impact of lithium/electrolyte plasticity on exchange current (March, 2017).

Completed

- Go/no-go: Combine plasticity with transport of lithium ions within the electrode electrolyte system. Otherwise, consider only elastic deformation of lithium/electrolyte (June, 2017).

Completed

- Report on the electrolyte shear modulus to prevent dendrites. (September, 2017).

Completed

- Incorporate SEI layer in lithium metal dendrite model (December, 2017).

Completed

- Evaluate the impact of mechanical properties and thickness of SEI layer on propensity of dendrite growth (March, 2018).

Completed

- Develop a model to evaluate the precipitation process of lithium-sulfide during battery discharge (June, 2018).

In progress

- Develop a model for surface morphology evolution in sulfur cathode (September, 2018).

In progress

Sept 2016 | Dec 2016 | March 2017 | June 2017 | Sept 2017 | Dec 2017 | March 2018 | June 2018 | Sept 2018

APPROACH

Identify problem:

1. Li plating
2. Lithium sulfide deposition

Thermodynamics
Kinetics
Mass-transport

Develop continuum and phase-field model

Mechanical

Literature/Data

Obtain material parameters (equilibrium, transport etc.)

Validate Model against data

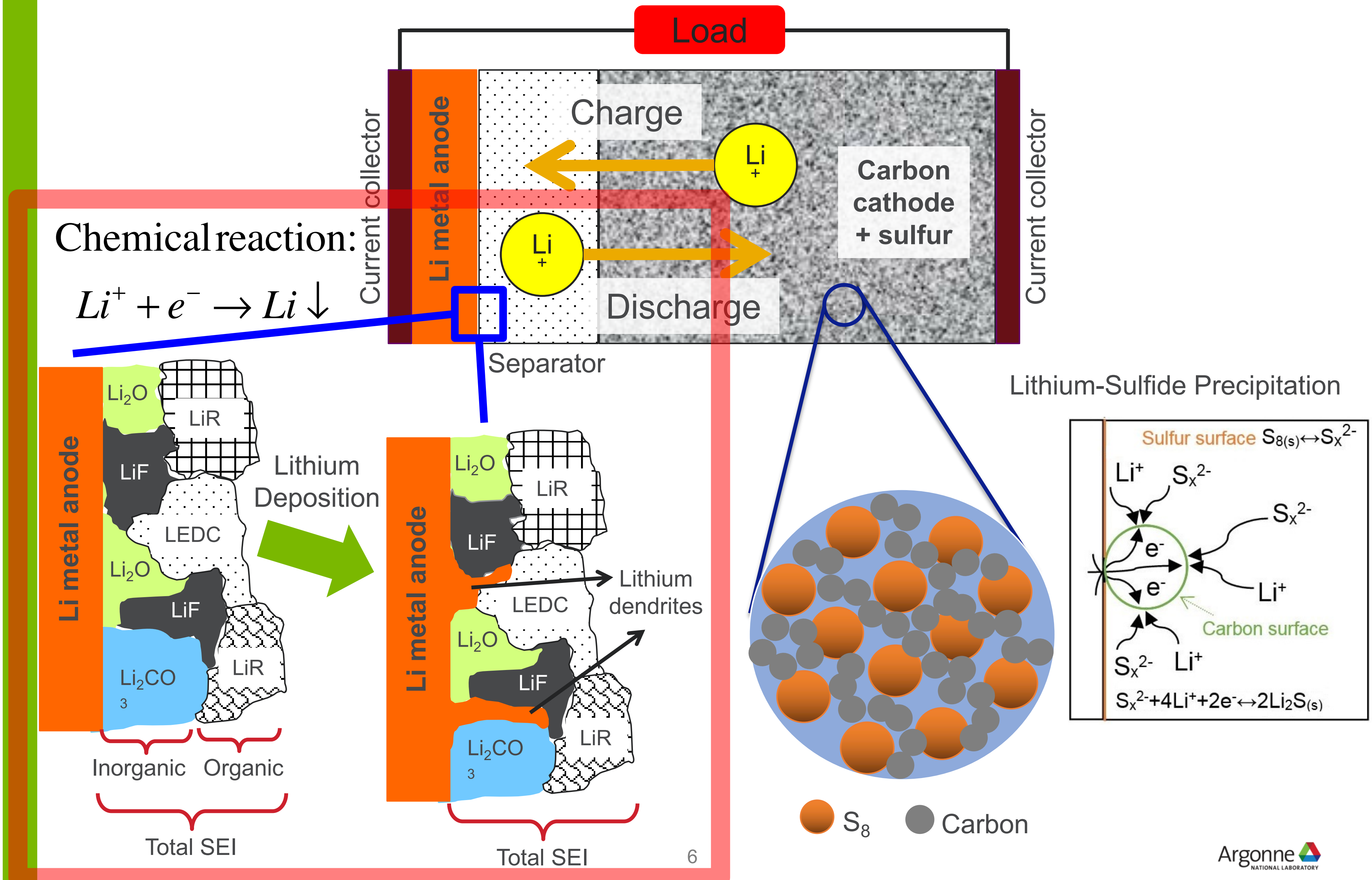
- Identify limitations
- Guide improvements
- Test hypothesis

Use model to understand impact of SEI layer on dendrite growth and evaluate strategies to minimize cathode surface passivation due to lithium sulfide precipitation.

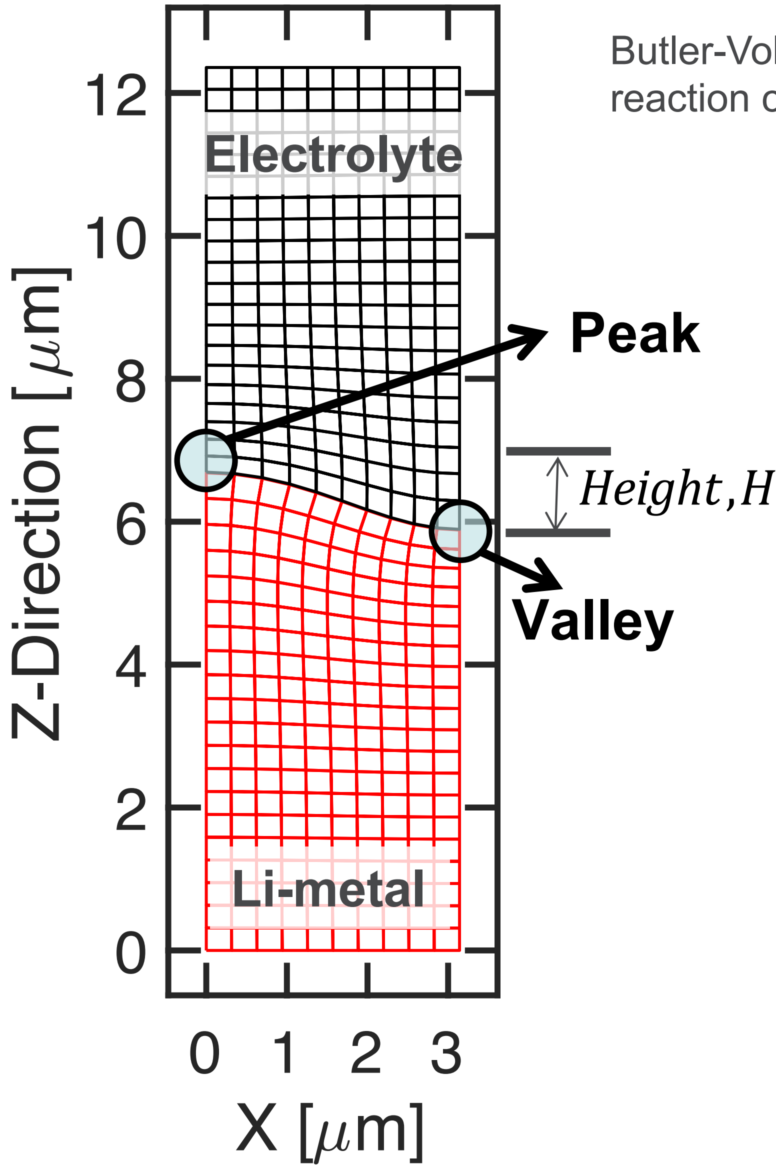
Guide electrode design: Formation of stable SEI layer and strategies to minimize surface passivation.

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

DEPOSITION: AN ISSUE AT ANODE AND CATHODE

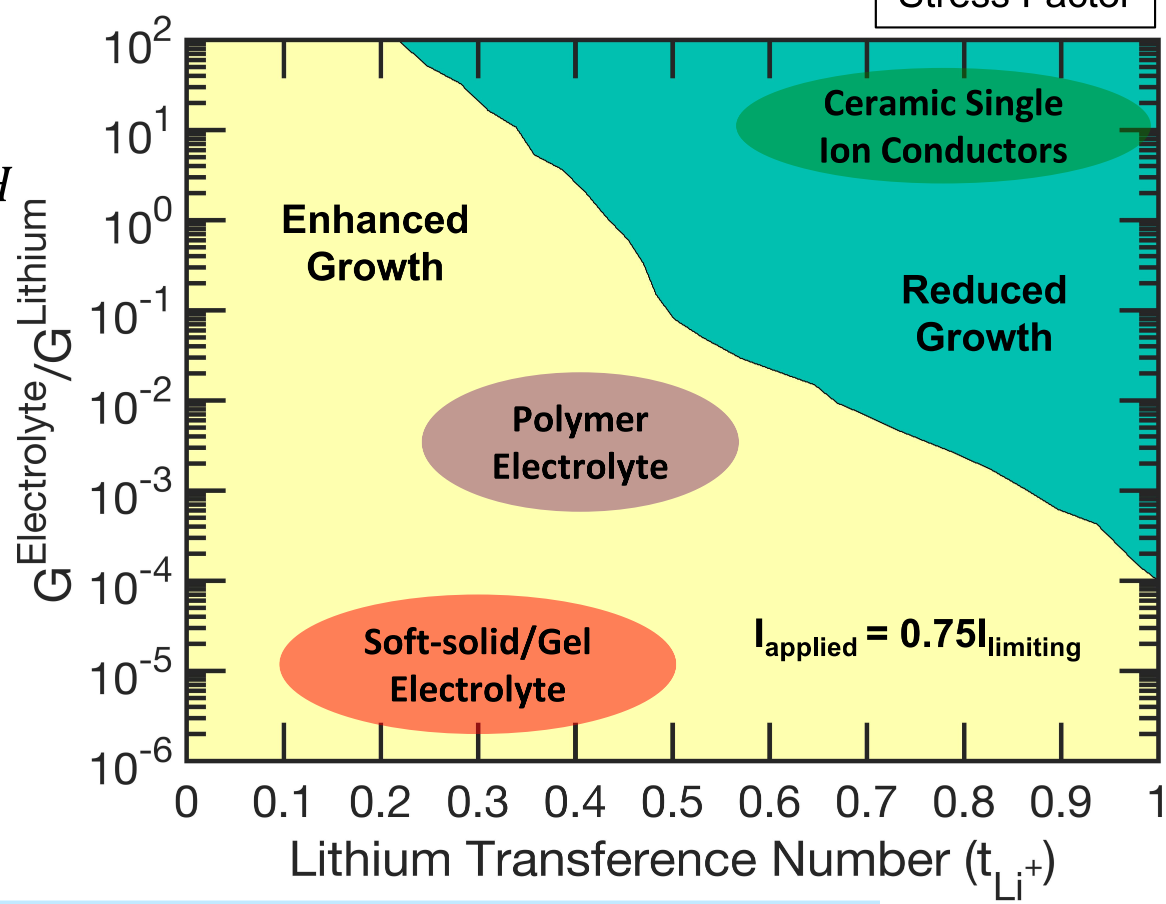


PREVIOUS YEAR PROJECT ACCOMPLISHMENTS



Butler-Volmer reaction current:

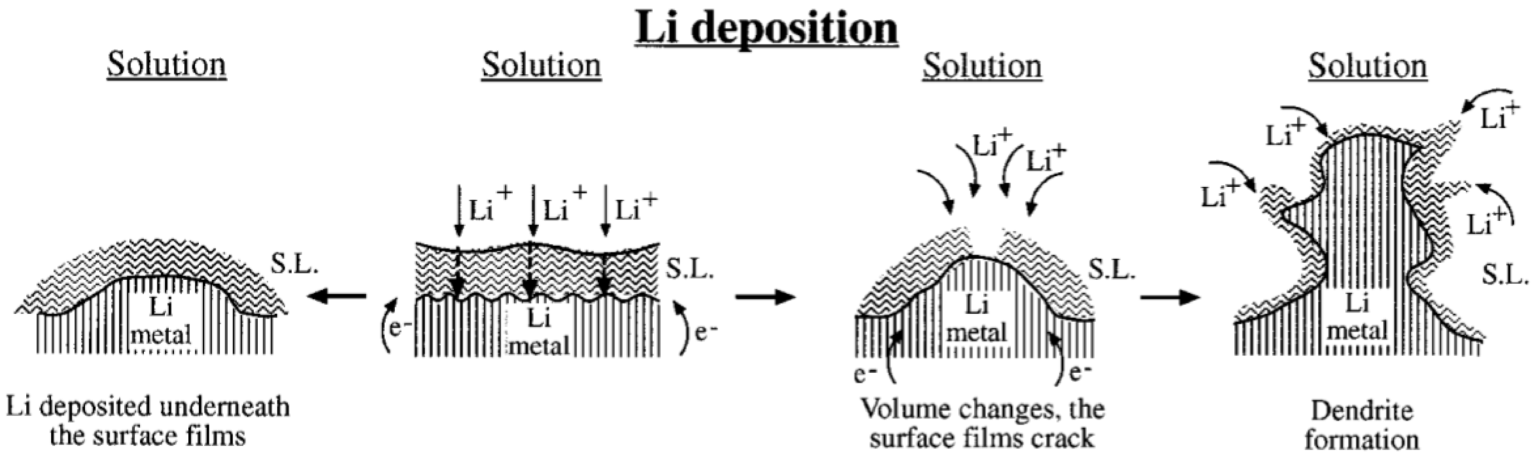
$$i_{BV} = \underbrace{F k_a^{\alpha_c} \left(k_c c_e\right)^{\alpha_a} \left[\exp\left(\frac{F\eta}{2RT}\right) - \exp\left(\frac{-F\eta}{2RT}\right)\right]}_{\text{Concentration/Overpotential Factor}} \cdot \underbrace{\exp\left(\frac{\Delta\mu_{e^-}}{2RT}\right)}_{\text{Mechanical Stress Factor}}$$



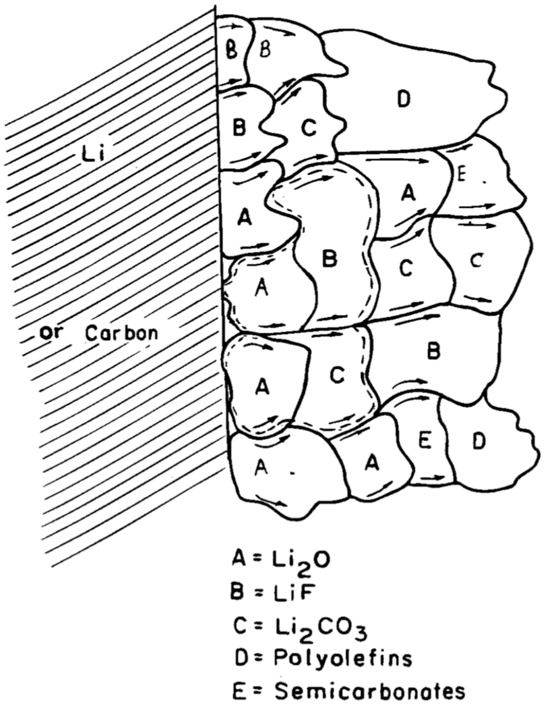
- **Impact of SEI layer was not taken into consideration.**

MODELING DENDRITE GROWTH WITH SEI LAYER

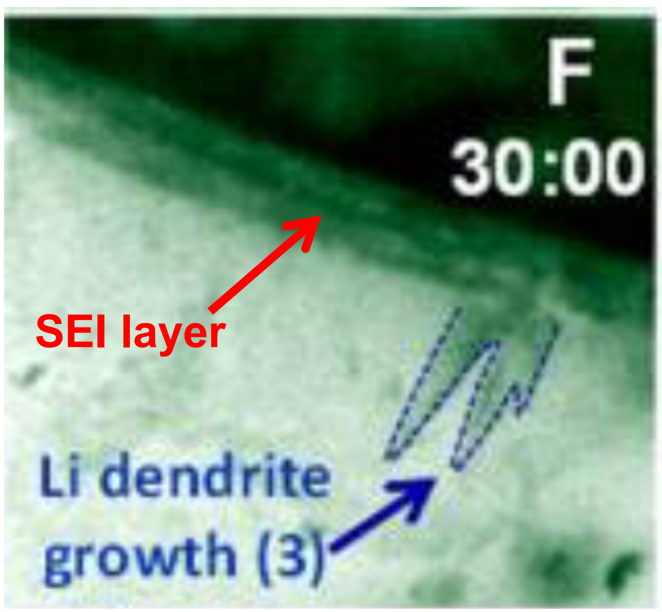
How does the SEI layer impact overall dendrite growth process?



Y. S. Cohen, Y. Cohen, and D. Aurbach. *J. Phys. Chem. B* 2000 104 12282 – 12291.



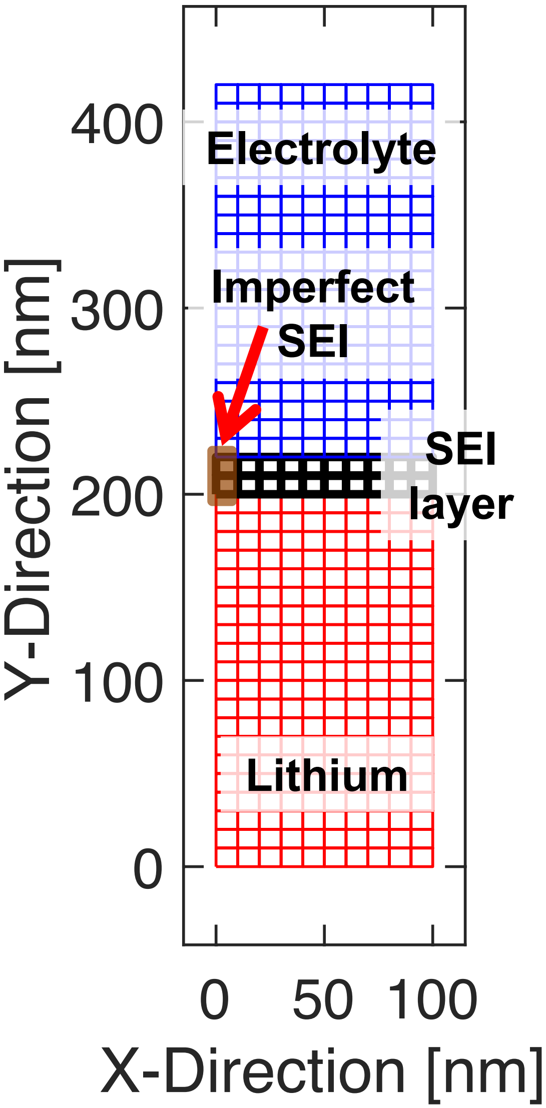
Peled et al., *JES* (1997) L208



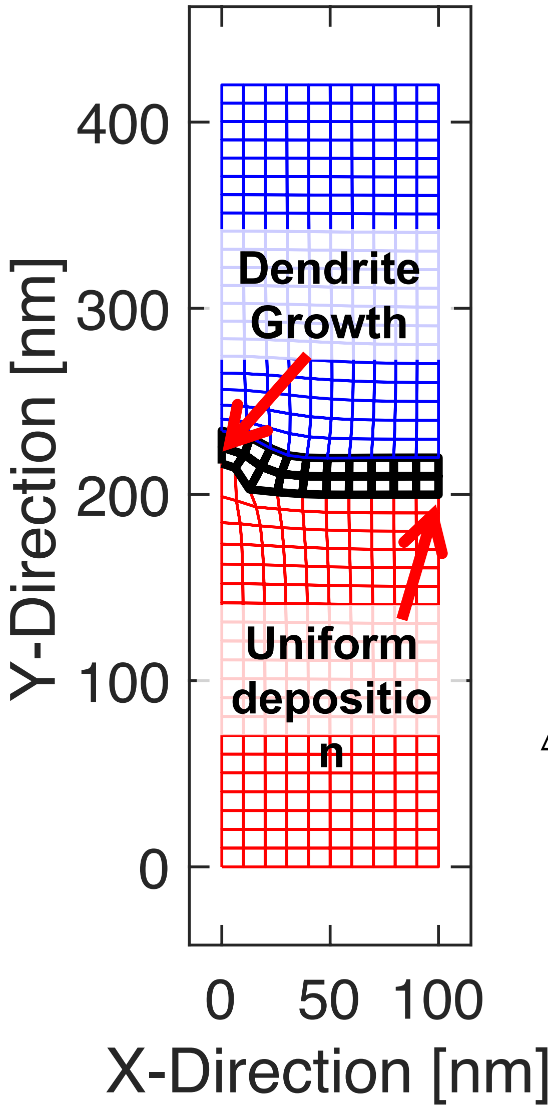
Zeng et al., *Nano Letters* (2014) 14 1745 - 1750

- Non-uniform transport through SEI and its fracture plays a major role in lithium dendrite growth.

BUILDING SEI ON "NEWMAN MODEL"



Before Dendrite Growth



Formation of a Dendritic Nucleus

Journal of The Electrochemical Society, **152** (2) A396-A404 (2005)
0013-4651/2005/152(2)/A396/9/$7.00 © The Electrochemical Society, Inc.

The Impact of Elastic Deformation on Deposition Kinetics at Lithium/Polymer Interfaces

Charles Monroe*,z and John Newman**

$$i_{BV} = \left\{ \begin{array}{l} Fk_{ref}\left(c_e\right)^{\alpha_a} \exp\left(\dfrac{\alpha_a \Delta\mu_{e^-}}{RT}\right) \cdot \\ \left[\exp\left(\dfrac{\alpha_a F\eta_s}{RT}\right) - \exp\left(-\dfrac{\alpha_c F\eta_s}{RT}\right)\right] \end{array} \right\}$$

$\Delta\mu_{e^-}$ Mechanical stress induced change in electrochemical potential:

- **Surface curvature**
- **Compressive stress**
- **Shear stress**

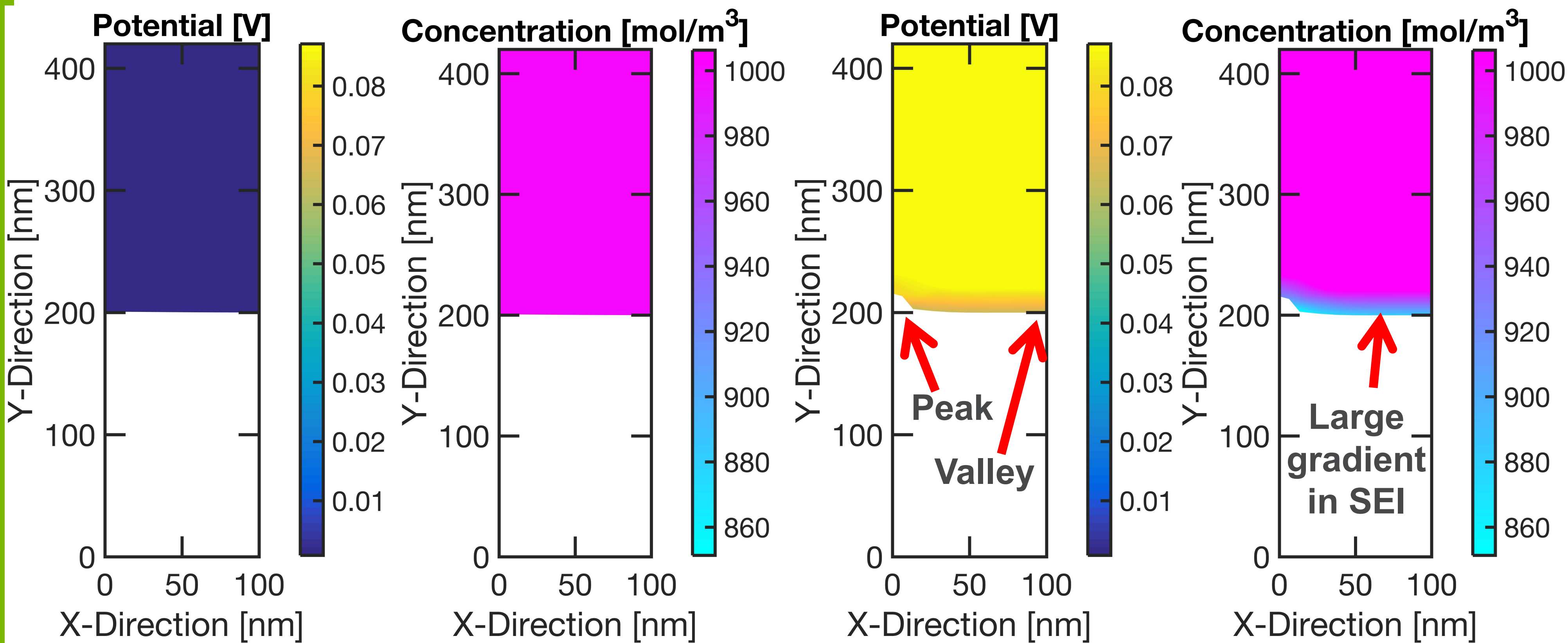
- Compressive stress leads to lowering of reaction current.
- As compression increases at the tip, deposition occurs in the valley and suppresses dendrites.

CONCENTRATION AND POTENTIAL PROFILE

$$\left(G^{SEI}/G^{Li}\right)\sim 1.0 \qquad \delta_{SEI}\sim 20nm \qquad \gamma \sim 0.1 J/m^2$$

$I_{applied} \sim 1A/m^2 = 0.1mA/cm^2$

$I_{applied} \sim 100A/m^2 = 10mA/cm^2$

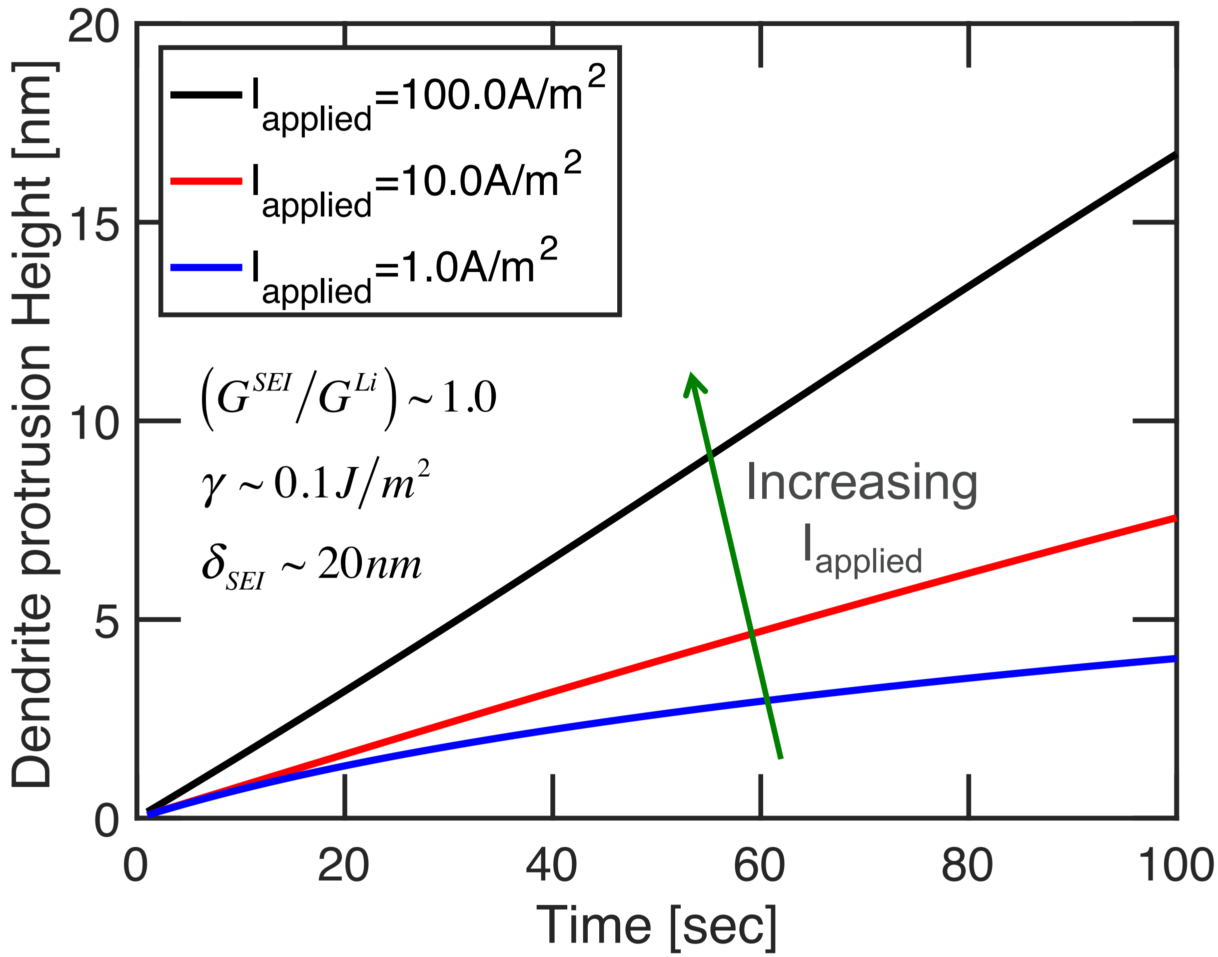


- No nucleation of dendritic protrusion during deposition at lower rates.

- Lithium nucleus formation and growth of dendritic protrusion at high current.

IMPACT OF APPLIED CURRENT DENSITY ON LITHIUM DENDRITE GROWTH

Increasing current density → Dendrite growth



- Enhanced potential and concentration gradients at higher current density leads to growth of dendritic protrusion

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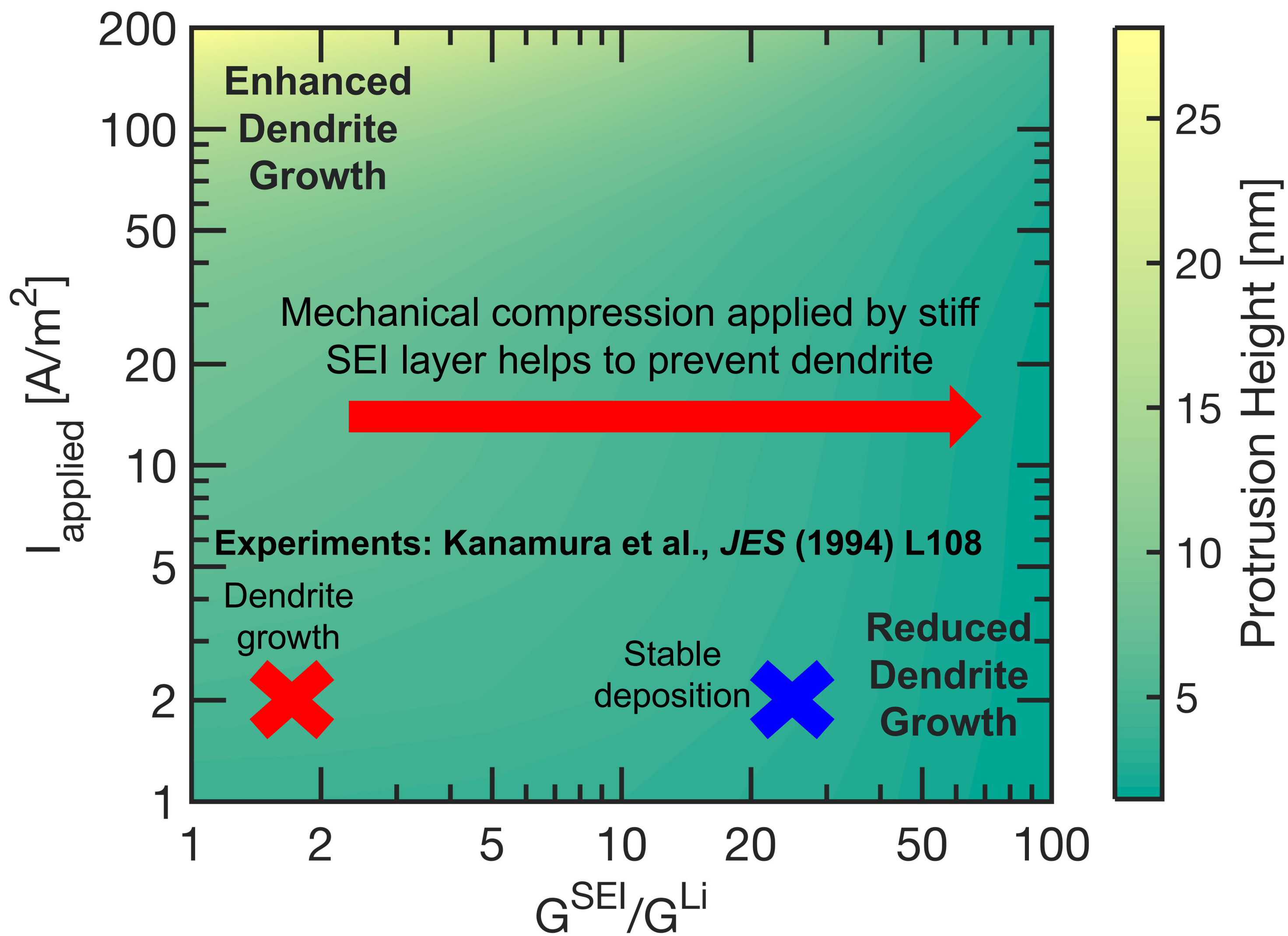
PHASE MAP BETWEEN CURRENT DENSITY AND SEI STIFFNESS REGARDING DENDRITE GROWTH



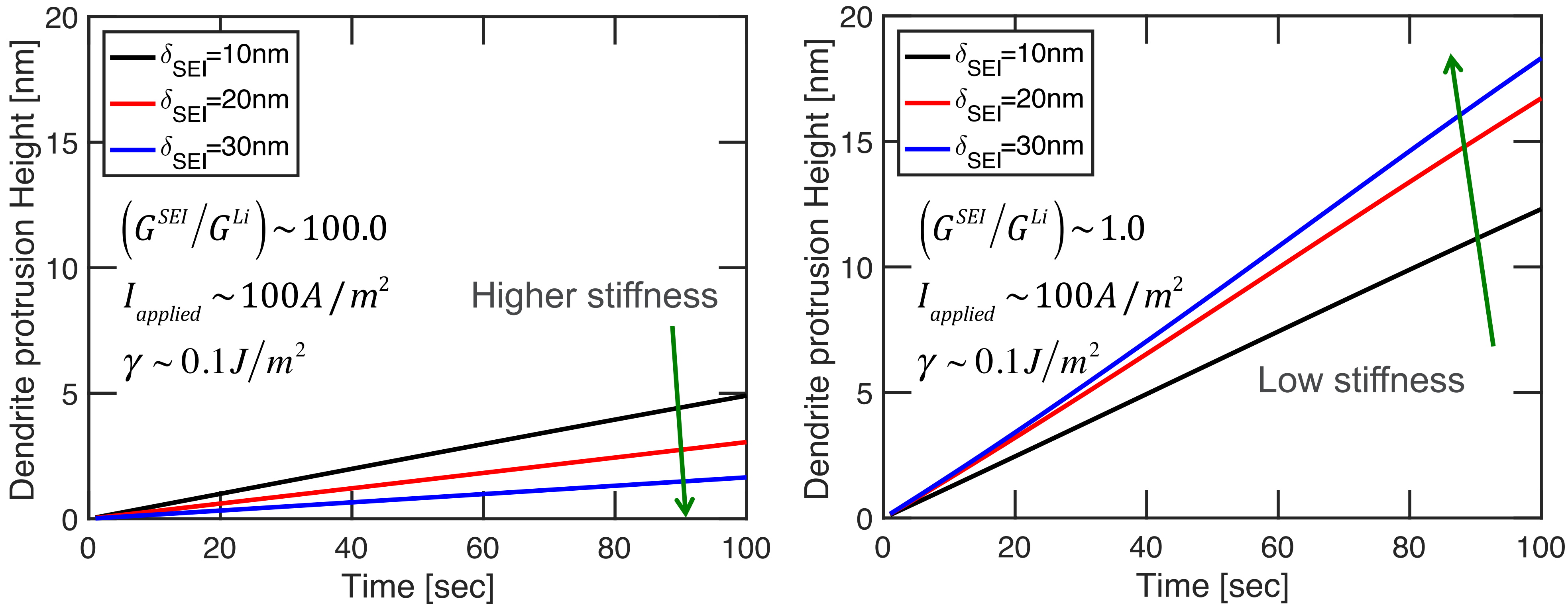
$\gamma \sim 0.1 J/m^2$

$\delta_{SEI} \sim 20nm$

- Significant suppression of dendrites for SEI layer with large SEI stiffness.

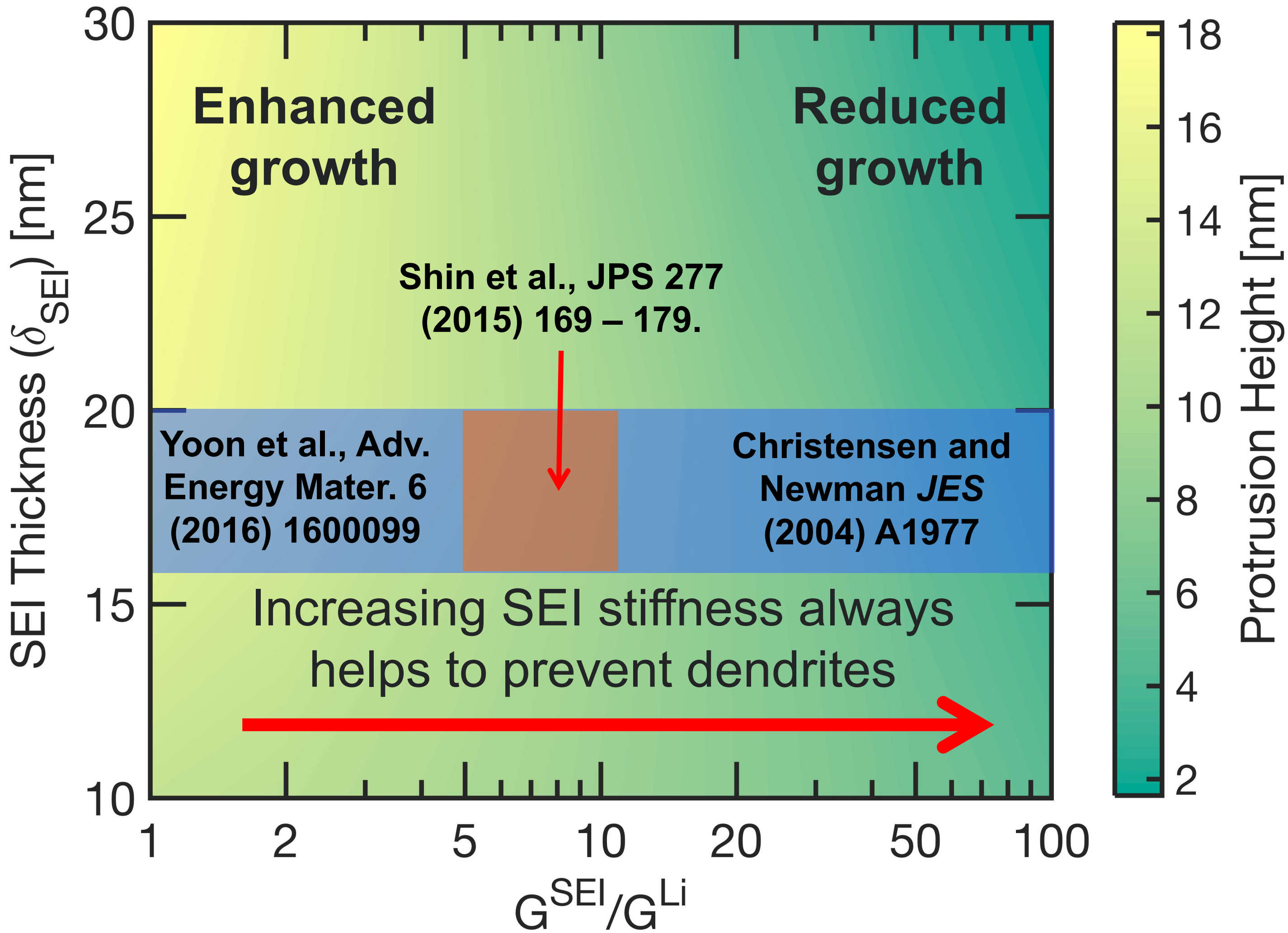
IMPACT OF SEI THICKNESS

- SEI layer thought to have higher stiffness and lower conductivity and diffusivity as compared to the electrolyte.



- Stiff SEI layers apply high compressive force on dendritic protrusions. Increasing thickness of stiff SEI layers help to prevent dendrites.
- Increasing thickness of soft SEI leads to higher concentration gradient induced overpotentials, which lead to growth of dendritic protrusions.

PHASE MAP DEMONSTRATING EFFECTIVENESS OF SEI STIFFNESS AND THICKNESS

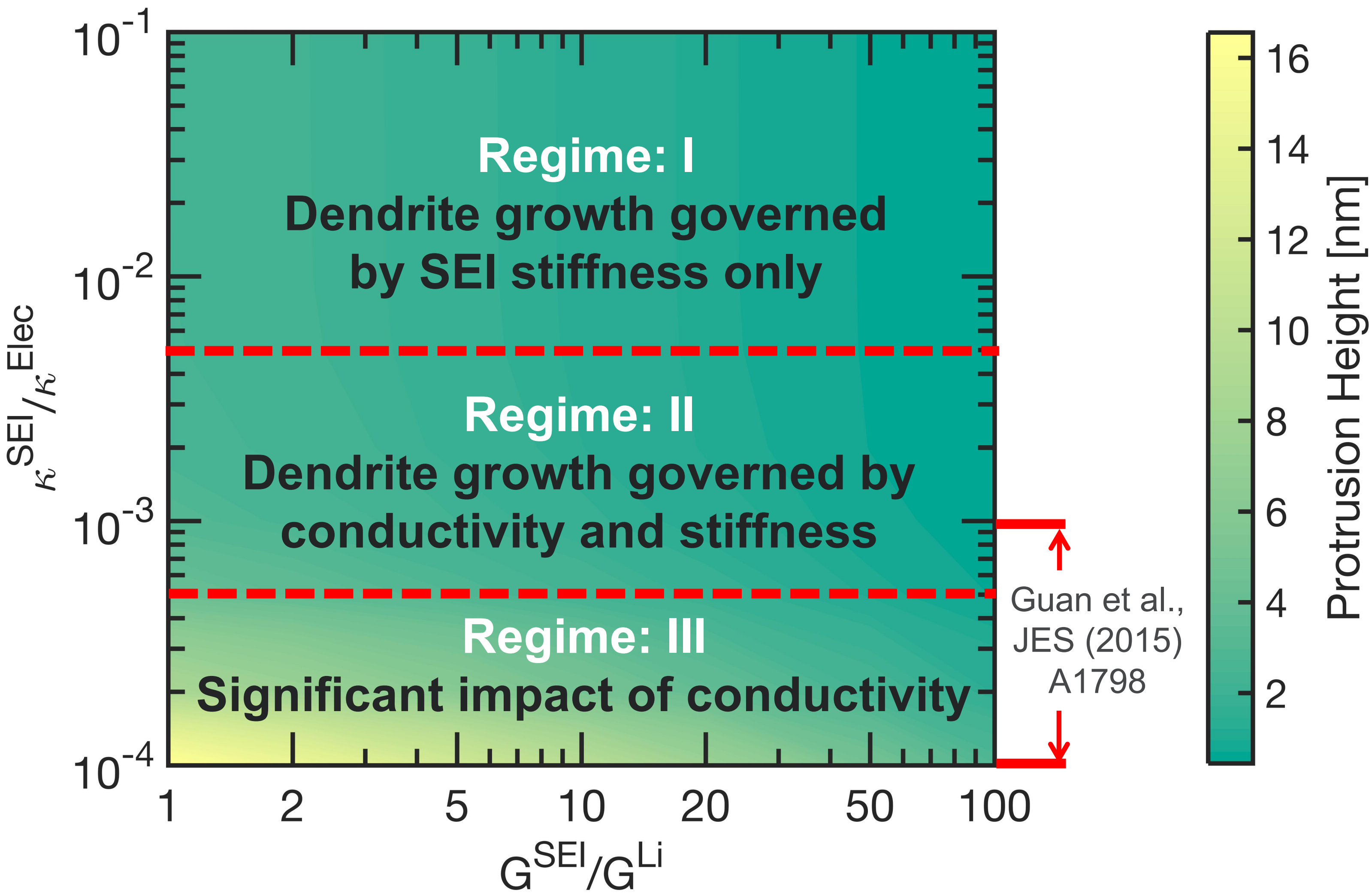


$I_{applied} \sim 100 A/m^2$

$\gamma \sim 0.1 J/m^2$

- SEI thickness and stiffness need to be optimized to ensure stable deposition, but with minimum impact on cell impedance.

COMBINED IMPACT OF CONDUCTIVITY AND STIFFNESS OF SEI ON DENDRITE GROWTH



$I_{applied} \sim 100A/m^2$

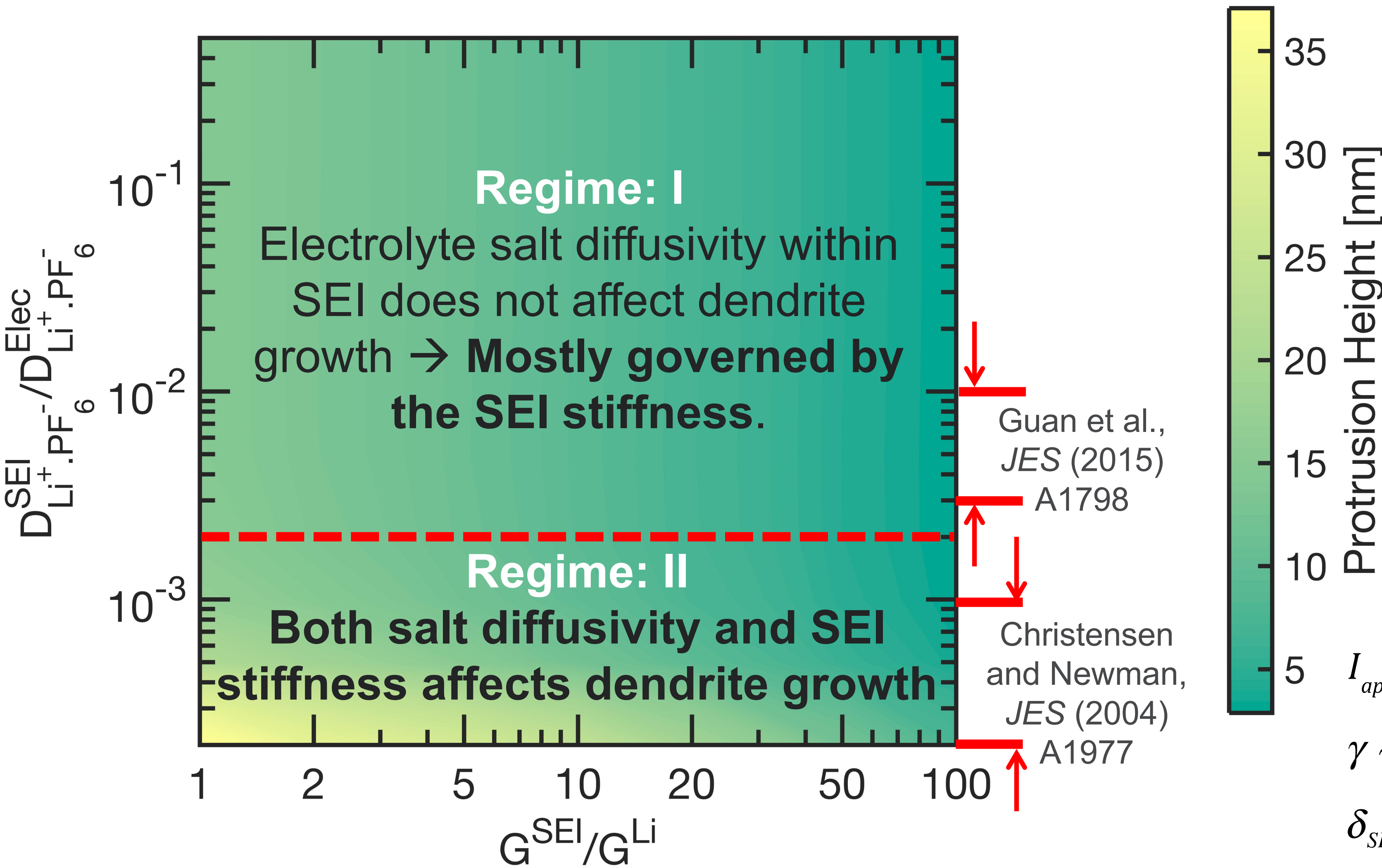
$\gamma \sim 0.1J/m^2$

$\delta_{SEI} \sim 20nm$

$\left(D^{SEI}/D^{Elec}\right) \sim 10^{-3}$

- Conductivity in SEI layer affects the dendrite growth process only if it is three orders of magnitude, or more, smaller than that of electrolyte.

IMPACT OF LITHIUM DIFFUSIVITY AND STIFFNESS OF SEI LAYER ON DENDRITE GROWTH



$I_{applied} \sim 100A/m^2$

$\gamma \sim 0.1J/m^2$

$\delta_{SEI} \sim 20nm$

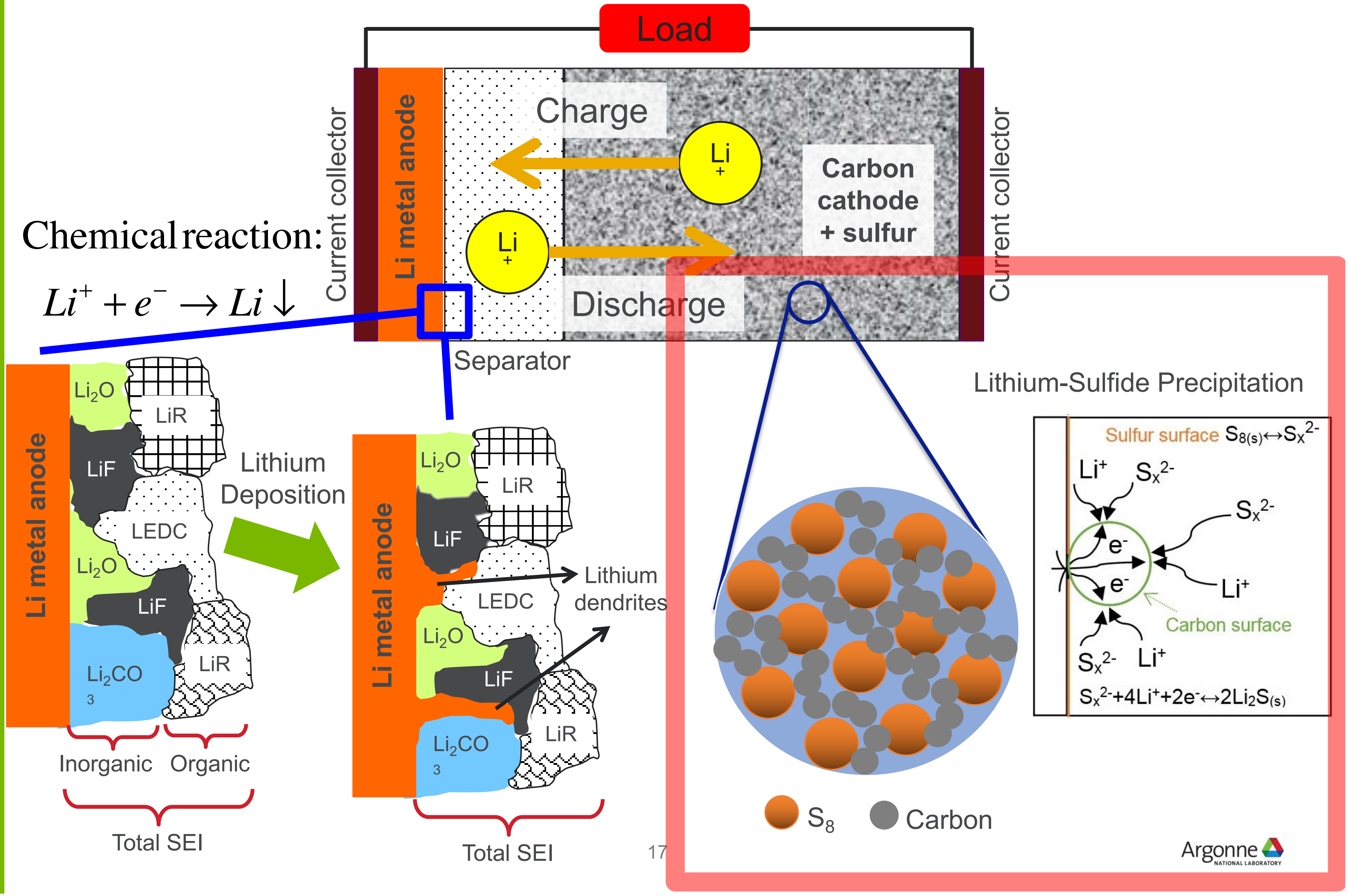
- Electrolyte salt diffusivity within SEI layer starts to affect dendrite growth if it is much smaller than salt diffusivity within the electrolyte.

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

DEPOSITION: AN ISSUE AT ANODE AND CATHODE

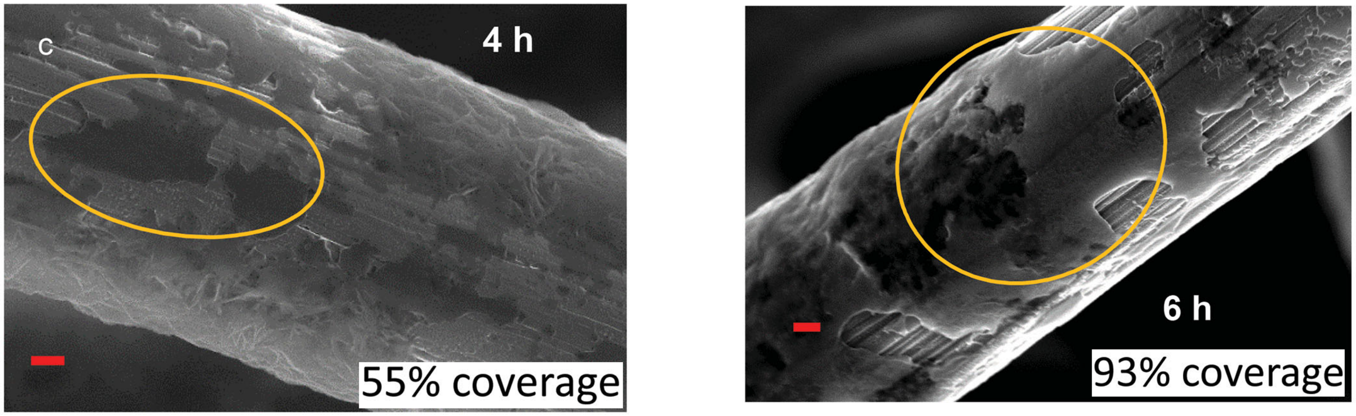
Chemical reaction:

$$Li^{+} + e^{-} \rightarrow Li \downarrow$$

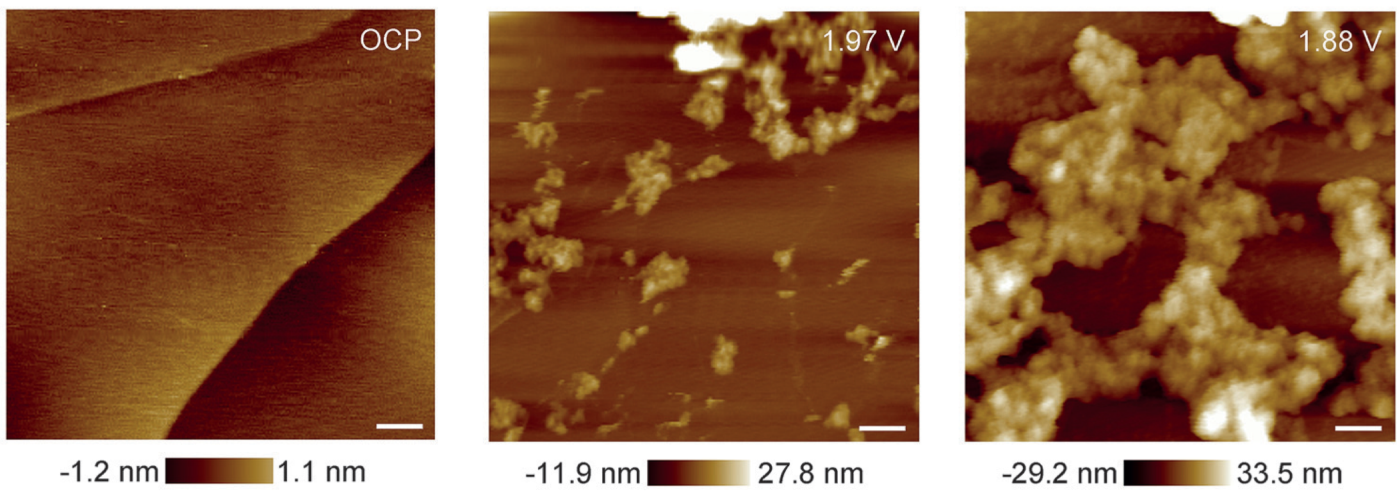


LI2S PRECIPITATION IN LI-S BATTERY

- SEM image of Li_2S on Carbon fiber in discharge [1]:



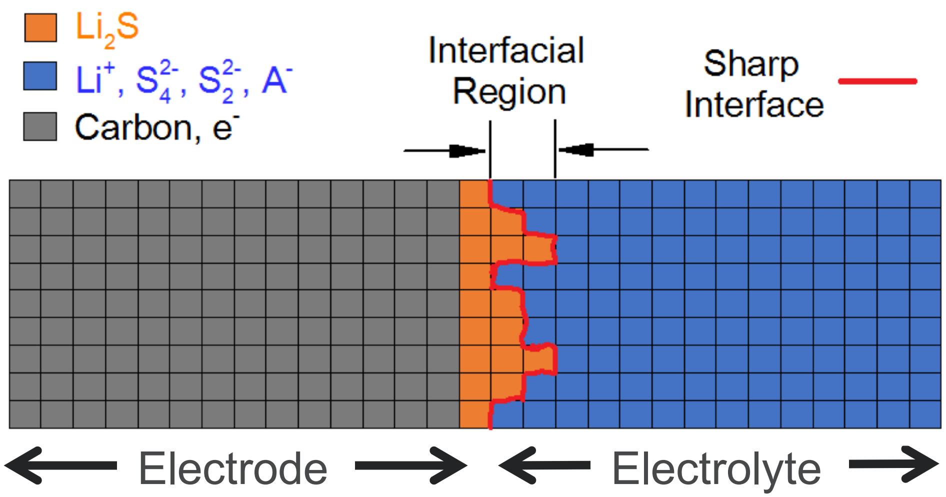
- In Situ AFM topography images of Li_2S on graphite surface [2]:

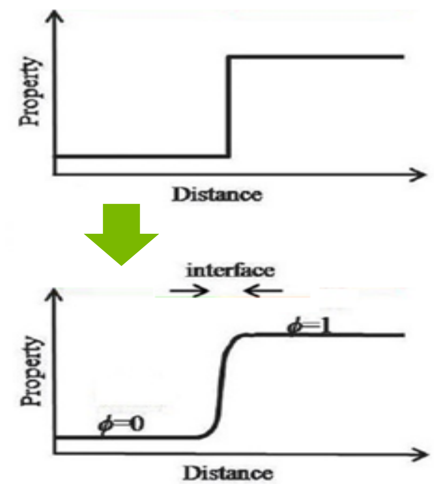


[1] Fan et al., Advanced Materials, 27, 2015, 5203-5209;
[2] Lang et al., Angew.Chem.Int.Ed., 55, 2016, 15835-15839

PHASE FIELD MODELING

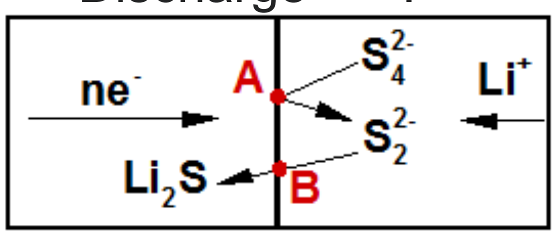
- Simulate and evaluate the Li_2S precipitation process in the discharge-charge:





- Assumptions: 1) Li_2S is the only solid product; 2) Li_2S nucleation is neglected in the electrolyte: 3) For simplicity, partly discharge-charge process is applied between S_4^{2-} and Li_2S:

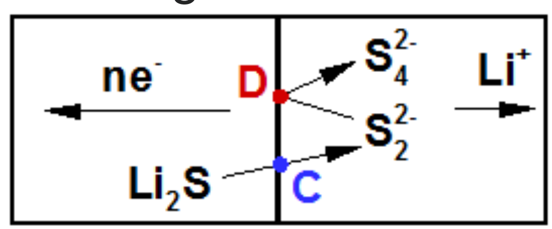
Discharge[1,2,3]:



A: $S_4^{2-} + 2e^- \rightarrow S_2^{2-}$

B: $S_2^{2-} + 4Li^+ + 2e^- \rightarrow Li_2S$

Charge [1,4,5]:



C: $2Li_2S + S_4^{2-} \rightarrow 3S_2^{2-} + 4Li^+$

D: $2S_2^{2-} \rightarrow S_4^{2-} + 2e^-$

[1] Want et al., JES 162 (3) A474, 2015
[2] Kawase et al. PCCP 2014, 16, 9344
[3] Kumaresan et al. JES 155 (8) A576, 2008
[4] Cuisinier et al. Phy.Chem. Letter, 4(2013), 3227.
[5] Lang et al. Angew. Chem. Int. Ed. 55(2016), 15835

EQUATIONS USED FOR MODEL

- Governing equations:

  1) Material Balance [1,2]: $\frac{\partial c_i}{\partial t} = -\nabla \cdot f_i \pm a_i \sum s_i r$ $\qquad f_i = -\frac{D_i c_i}{k_B T} \nabla \frac{\delta G}{\delta c_i}$

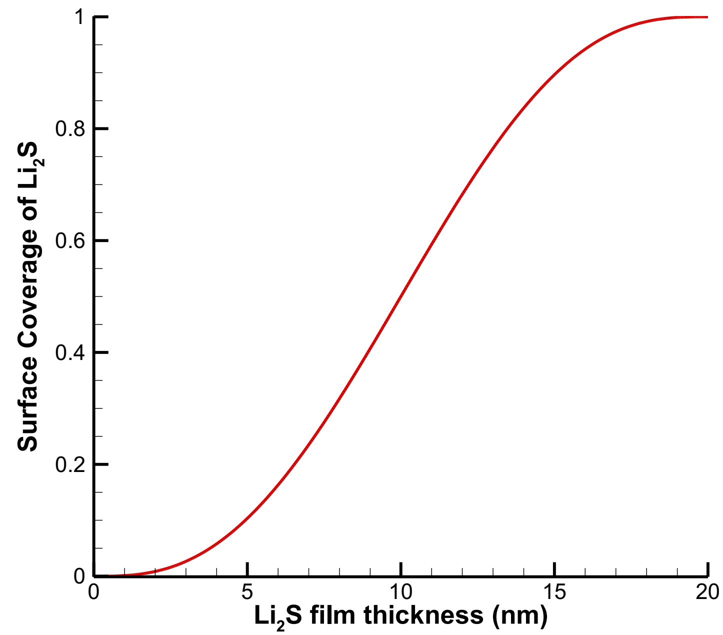
  2) Potential field [3]: $-\sigma(\xi)\nabla^2 \phi = F \sum_{i=1}^{n} z_i c_i$ $\qquad \sigma(\xi) = \sigma_{eff}\xi + \kappa_{eff}(1-\xi)$

  3) Phase parameter [2]: $\frac{\partial \xi}{\partial t} = \frac{\partial \tilde{c}_{Li_2S}}{\partial t} = r\left(\frac{\delta G}{\delta \tilde{c}_{Li_2S}}\right)$ $\qquad \tilde{c}_{Li_2S} = c_{Li_2S} / c_{Li_2S}^{ref}$

- Li_2S surface coverage variation [4]:

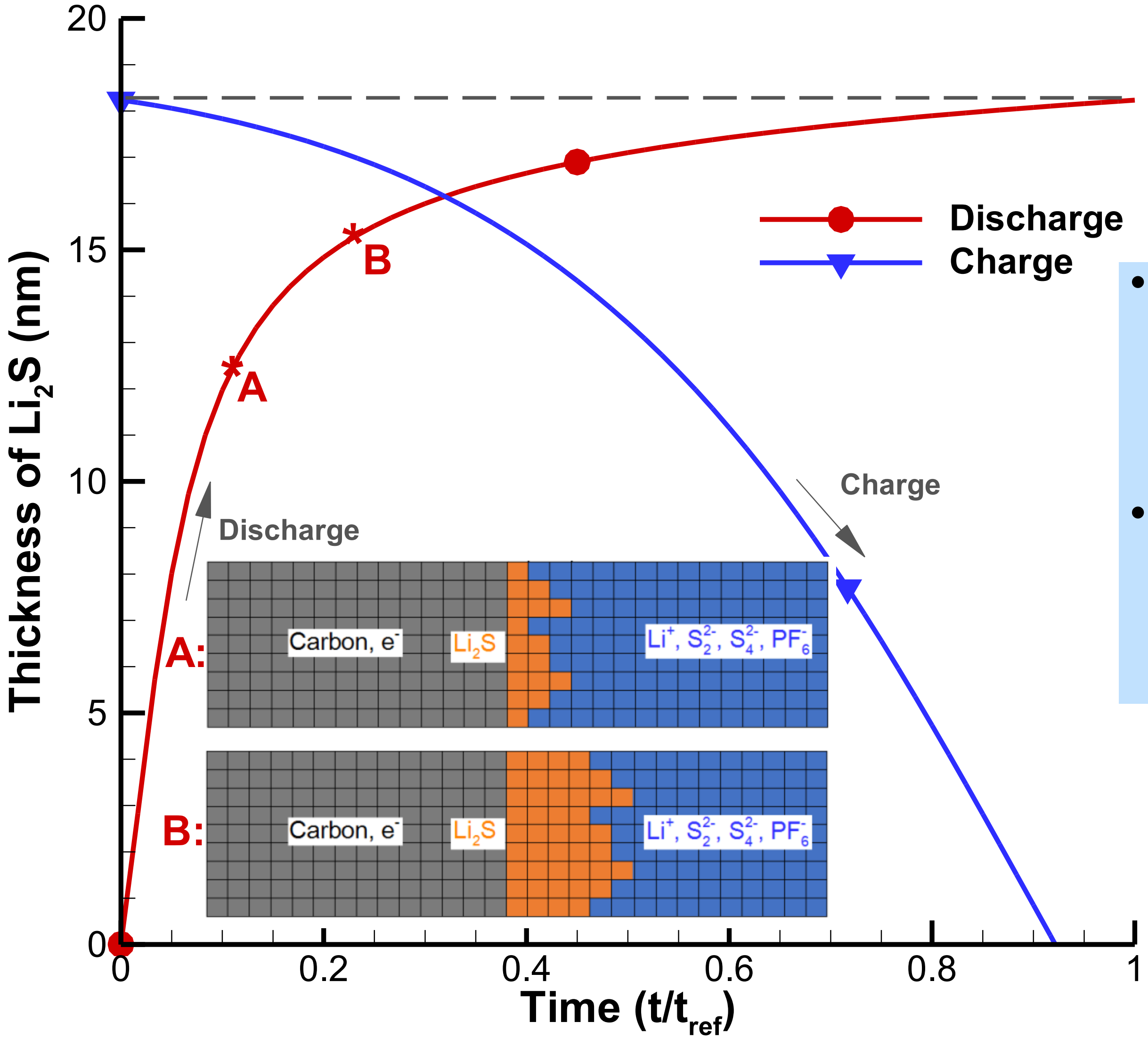
$$S(x) = \left(\frac{x}{x_0}\right)^3 \left(6\left(\frac{x}{x_0}\right)^2 - 15\left(\frac{x}{x_0}\right) + 10\right)$$

$$S(x)\big|_{x=0} = 0 \qquad S(x)\big|_{x=x_0} = 1$$



[1] Ferguson et al. JES, 159(12), A1967, 2012;
[2] Bazant et al. Acc. Chem. Res., 46(5), 2013, 1144;
[3] Deng et al. JES, 160(3), A487, 2013.
[4] Liu et al. App. Mat. & Inter., 9, 2016, p5263;

LITHIUM SULFIDE FILM GROWTH



- Li2S film growth (on discharge) and dissolution (on charge) follow different trends;
- This originates from the different redox mechanism of Li2S on the active carbon surface.

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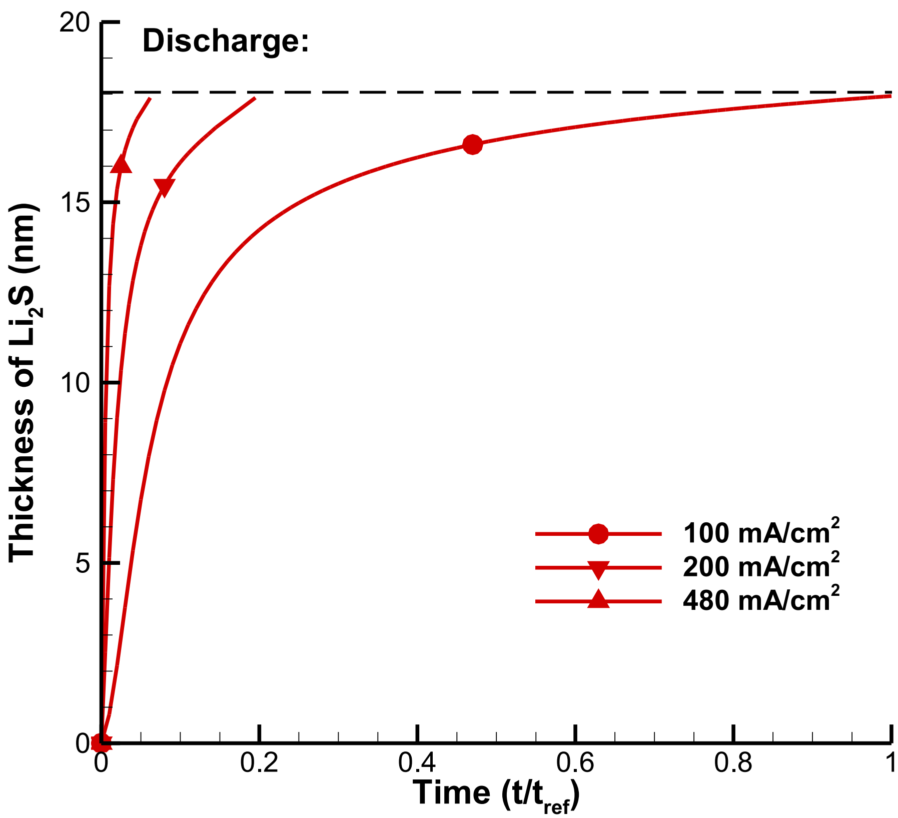
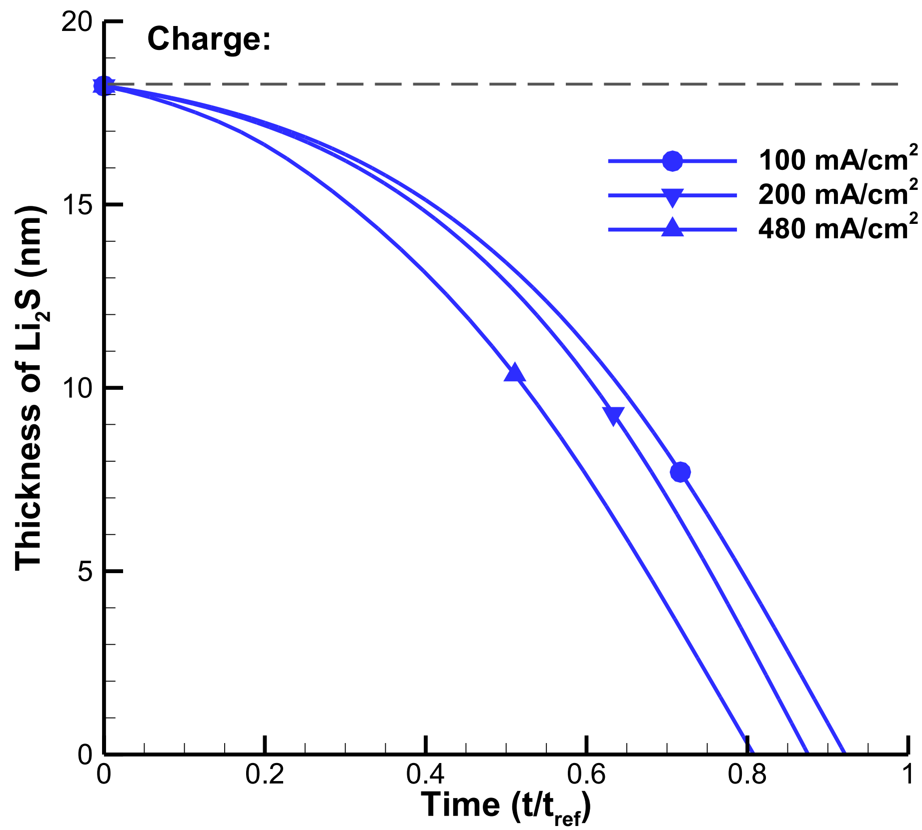
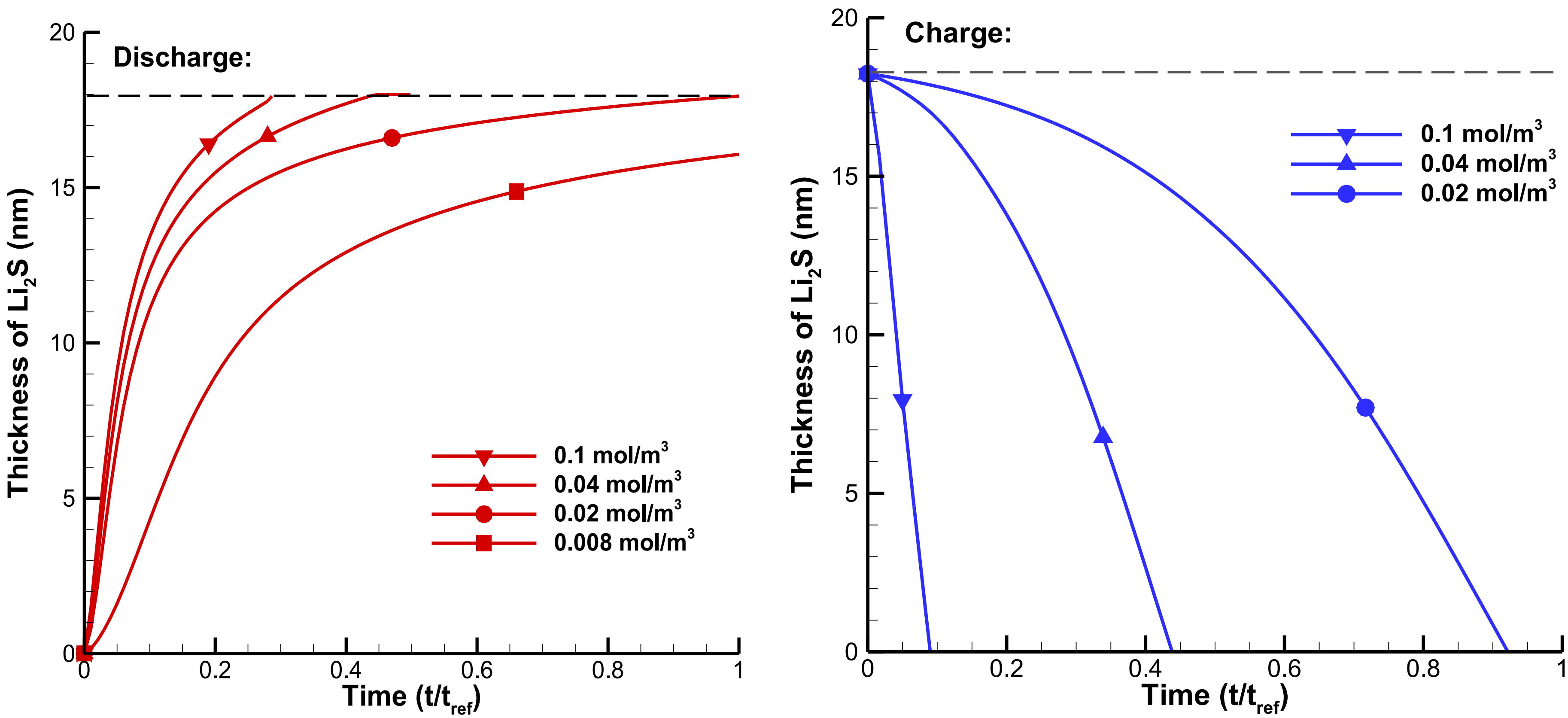
EFFECT OF CHARGE-DISCHARGE RATE





- Model shows different C-rate (electron flux) can lead to different time needed for Li2S film growth and removal. A consequence of the different reaction path between charge and discharge.

EFFECT OF S_4^{2-} SOLUBILITY



- Low S_4^{2-} solubility in electrolyte can significant slow down the Li_2S growth

RESPONSE TO PREVIOUS YEAR REVIEWER'S COMMENTS

- The previous year's work was on lithium dendrite growth. Hence all the comments focused only on the lithium metal work.
  - This is the first year for the lithium-sulfide precipitation work.

- All the reviewers appreciated the flexibility of the detailed model being developed for understanding the lithium dendrite growth under the influence of mechanical stress, which is usually observed in solid electrolytes (polymer and ceramic).

- However, a general agreement was observed among the reviewers that more experimental data collection is required for successful completion of the project.
  - In response, we have started to collaborate with Prof. Shrayesh Patel from University of Illinois, Chicago for conducting relevant experiments regarding lithium deposition with polymer electrolyte.

- Regarding the future work, the reviewers suggested to narrow down the possible efforts and focus into it more deeply.
  - In response, we have decided to focus more into the issues associated with solid-electrolyte-interphase (SEI) formation, and its impact on stabilization of lithium nucleus formation.

COLLABORATION AND COORDINATION

- LBNL
  - Kenneth Higa
  - Nitash Balsara

- DOE User Facility
  - Advanced Light Source (ALS), located in LBNL
  - Advanced Photon Source (APS), located in ANL

- ANL
  - Marius Stan

REMAINING CHALLENGES AND BARRIERS

- **Lithium metal deposition and dendrite growth in anode:**
  - Estimation of mechanical and transport properties through the SEI layer on top of lithium metal.
  - Impact of fracture in the SEI layer on lithium dendrite growth.
  - Elucidation of dendrite growth in ceramic electrolytes with grain/grain-boundary microstructure.

- **Lithium-sulfide precipitation and carbon surface passivation in cathode:**
  - Incorporation of complicated sulfur electrode micro-structure into the model.
  - Nucleation of Li_2S in the electrolyte is neglected, which results in very difficult quantitative comparisons with reality.
  - The interfacial region width is an adjustable parameter and depends on the applied energy barrier height and gradient energy coefficient, which both are difficult to be obtained through experiment.

PROPOSED FUTURE WORK

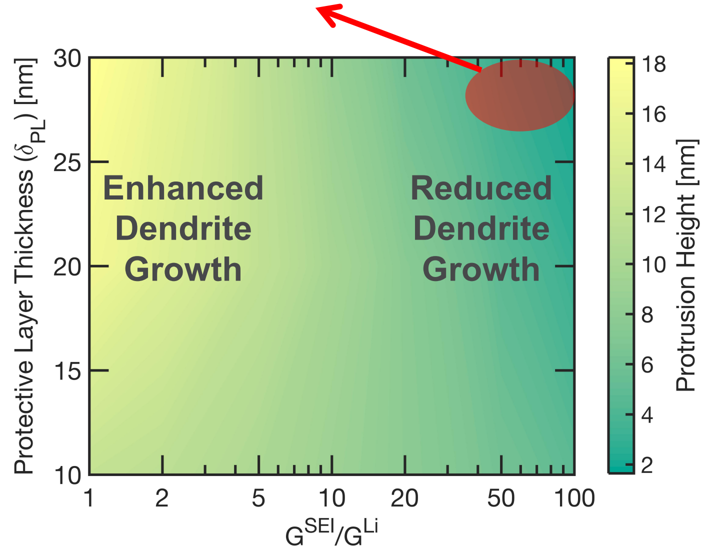
- **Lithium dendrite growth on anode:** Improve model prediction for the dendrite growth process.
  - Obtain relevant mechanical and transport properties from appropriate experiments.
  - Update computational model to incorporate the possibility of fracture within the SEI layer and investigate its impact on the overall lithium dendrite growth process.

- **Lithium-sulfide precipitation on cathode substrate:** Develop a two dimensional or three dimensional model to study the sulfur electrode structure evolution:
  - Develop appropriate microstructure of sulfur electrode from experiment for 2D and 3D phase field model.
  - Model the surface morphology evolution in the discharge and charge process of the electrode.
  - Evaluate the impact of different sulfur electrode structure on the electrode performance.

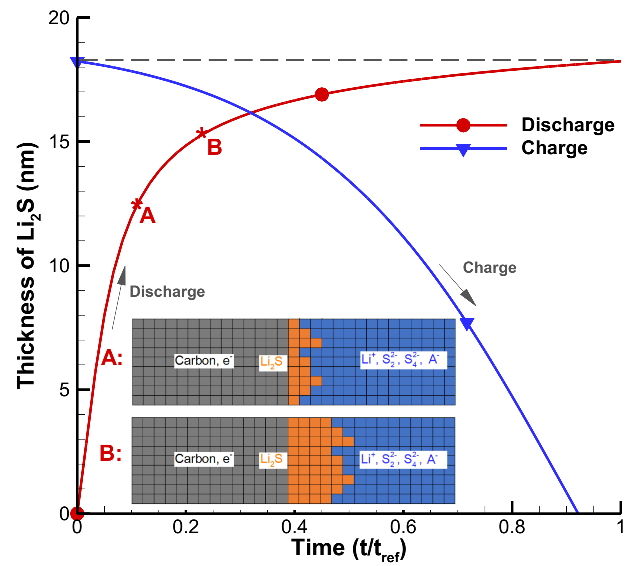
SUMMARY

- Impact of solid electrolyte interphase (SEI) layer on lithium deposition and dendrite growth process has been investigated.
  - Increasing stiffness of the SEI layer helps to delay the growth of dendrites.
- If a protective layer (PL) is used to prevent the growth of dendrites, and transport through the protective layer is a limiting factor, optimum stiffness and thickness of PL is necessary for extracting the maximum effectiveness with minimum impact on performance.

Hollow carbon nano-sphere protective layer: Zheng et al., Nature Nanotechnology (2014) 618



- A phase field model is developed to evaluate the Li_2S precipitation process in the discharge of Li-S battery:
  - Surface passivation has been taken into consideration to model the high sulfur loading condition.
  - Modeling results indicate that Li_2S film growth and removal follows different trends, and high C-rate can potentially lead to Li_2S accumulation on the active carbon surface.



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